

Nanoheterogeneous palladium electrodeposits with anomalously high hydrogen-sorption ability: synthesis and properties

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Deposits of metal particles of nanoscale size are of great scientific interest, demonstrating different and sometimes novel properties as compared with bulk materials. Palladium deposits exhibiting high hydrogen sorption ability and good catalytic properties also attract high attention as a model of the role long-living defects play in sorption ability.

Properties of palladium deposits can be controlled by the deposition potential and the composition of the deposition solution. In this work, we have taken these two routes for obtaining palladium deposits of high hydrogen sorption abilities and high specific surface areas: the electrodeposition at different potentials and the so-called templating.

It is shown [1-3] that, by varying the deposition potential, three different types of Pd nanostructures can be synthesized. First of all, these are bulk-type deposits formed at low overvoltage under kinetic control (group 1); secondly, common palladium deposits forming under diffusion control at the potentials more positive than that of $\alpha \leftrightarrow \beta$ transition (group 2); and, thirdly, the deposits that demonstrated anomalous properties and were obtained at the potentials of β -phase formation (group 3).

STM technique demonstrated that all three groups of palladium electrodeposits are nanosize materials with wide size distributions of crystals with maximums, correspondingly, at 20 ± 2 , 40 ± 2 , 45 ± 2 nm. Within the groups, the distribution parameters vary smoothly with the deposition potential.

By comparing the specific area values experimentally found and calculated from STM results, it is concluded that substantial surface areas of the deposits of groups 1 and 2 are screened due to coalescence of crystals. The bulk content of structurally specific regions of intergranular boundaries is estimated in deposits of different types.

Deposits of group 3 are found to exhibit unusual sorption properties probably caused by strong lattice deformation of the metal during rapid and deep hydride formation in the course of their growth. Such anomalous deposits are formed in the deposition-potential range from 0.02 to 0.06 V (rhe) and are characterized by a high hydrogen content in the hydride α -phase and also an extremely high H/Pd atomic ratio. The latter approaches 1.2 at ca. 0.1-atm. effective pressure, whereas the corresponding ratio for conventional palladium materials never exceeds ~ 0.65 . The effective pressure of $\alpha \leftrightarrow \beta$ transition is lower as compared with “usual” deposits.

A self-consistent description of the sorption in α - and β -phases in terms of additive consideration of sorption by defective and defect-less regions is given [2-4]. The isotope H/D effect can be used for the general independent characterization of the defectiveness of Pd structure.

By comparing model and experimental sorption isotherms, the validity of the proposed approach is confirmed and the bulk content of defects in the studied materials is found to reach 25%. The highest defect content was observed for palladium deposits formed during active hydride formation (group 3).

An alternative approach, which suggests the uniformity of the matrix with specific properties that differ from those of crystalline Pd, is based on the use of Frumkin isotherm [5]. Fitting of experimental data by using this isotherm with the attraction constant of 2.0—2.1 demonstrates a satisfactory agreement. The problem of a formal contradiction of the classical treatment of β -phase region in terms of Temkin isotherm (which corresponds to repulsive interactions of hydrogen atoms in Pd bulk) with more general treatment in terms of Frumkin isotherm (which corresponds to attraction) is commented.

XRD study [6] of as-prepared and aged deposits confirmed the pronounced difference between the materials of groups 1, 2 and 3. For some types of samples the preferential crystallographic orientation (100) was observed. The deposited nanostructures have demonstrated the features of extended regions with disordered lattice.

Another novel approach of templating type was worked out, which elaborates the method [7]. The deposits were synthesized from solutions of H_2PdCl_4 containing additions of either polyethyleneglycol (PEG) or polyvinylpyrrolidone (PVP) at the potential of 0.25 V.

The hydrogen-sorption ability of these deposits resembled those of defective deposits obtained at the potentials of hydride formation. H/Pd ratios approached 1 for the case of PVP and exceeded 1 for PEG case. A high hydrogen content in the α -phase and the lower pressure of $\alpha \leftrightarrow \beta$ transition were also characteristics of these deposits.

The specific surface areas of deposits formed in PEG containing solutions approached $50 \text{ m}^2/\text{g}$, being calculated from copper and oxygen adsorption. The specific surface areas of both types of deposits increased with an increase in the polymer chain length.

Being subjected to long-term anodic—cathodic polarization, these deposits were found to undergo a certain aging process, during which they lost a part of their weight, but nonetheless did not lose their advanced properties. Their characteristics (S_{real} , H/Pd) even became slightly better, which confirmed the proposition that the polymers get incorporated into the structure of deposits and can dissolve during potential cycling.

The deposits formed in solutions with different polymers demonstrated different catalytic activities with respect to reduction of nitrate ions, those obtained from PVP-containing solutions being more active.

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